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(54) STABILISATION OF FLUOROCARBON POLYMERS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for improving the stability of high molecular weight fluorocarbon polymers.

U.S. Patent No. 3,085,083 discloses a process for converting the reactive end groups such as vinyl and carboxylate, of high molecular weight fluorocarbon polymers, such as tetrafluoroethylene/hexafluoropropylene copolymer, to the relatively unreactive $—CF_2H$ end group by subjecting the fluorocarbon polymer to relatively severe and lengthy heating in the presence of moisture. The severity of this treatment poses problems in processing.

In U.S. Patent No. 3,242,218, fluorocarbon polyether polymers are stabilised by decarboxylation and fluorination with fluorine. In this process, the polyether polymer is of low molecular weight and is treated in the liquid phase only, i.e. either as a liquid or dissolved in an inert solvent. In addition, these polyether polymers are characterized by having an ether oxygen which is beta to the carboxyl end group of the polymer and which has a known stabilizing effect to free radicals. In the decarboxylation reaction, the intermediate end group is the free radical $—O—CF_2$. The stability that the ether oxygen atom confers on this intermediate free radical end group was heretofore believed (formed from the precursor —COF end group) to be decarboxylated, leaving $—CF_2$. to unite with °F to form the stable end group $—CF_3$.

It has now been discovered that the stability of high molecular weight fluorocarbon polymers can be improved by exposing the fluorocarbon polymer in solid form and under relatively mild conditions and for relatively short periods of time to fluorine radicals.

According to the present invention, therefore, we provide a process for chemically stabilising a solid high molecular weight fluorocarbon polymer (as herein defined) which contains chemically unstable end groups which comprises contacting the solid polymer, in the absence of oxygen, with a source of fluorine radicals under conditions at which said source generates fluorine radicals, whereby at least 40% of the chemically unstable end groups are converted to chemically stable end groups.

By "fluorocarbon polymer" we mean a polymer which is either perfluorinated or highly fluorinated wherein any substituents other than fluorine are present at a frequency no greater than every other carbon atom in the main polymer chain.

The fluorine radicals react with the unstable end groups of the main polymer chain to convert them to a more stable form. This reaction is not limited to end groups, however, since sometimes polymers may contain unstable groups, for example unsaturated groups, within the polymer chain in which case the fluorine radicals also react to saturate these unstable internal groups. The unstable end groups which may be stabilised by the process of the present invention include carboxylate and vinyl end groups, such as disclosed in U.S. Patent No. 3,085,083 and other end groups which are convertible to a more stable form, for example $—CF_2H$ and amide groups. These end groups are detectable in the infrared spectrum of the polymer if the molecular weight of the polymer is not so high that the number of end groups present is too low to be detectable. Where the molecular weight is too high, the presence of unstable end groups

is suggested by anaology with the chemistry which leads to the formation of unstable end groups in fluorocarbon polymers of lower molecular weight wherein infrared analysis is applicable. Conversion of the infrared-detectable end groups is indicated by a decrease in, or disappearance of (depending on the degree of completion of the reaction), of the absorption intensity arising from the particular end groups originally present.

The end groups produced by the reaction with fluorine radicals are chemically stable, i.e. non-reactive, end groups, believed to be saturated fluorocarbon groups, specifically the $—CF_3$ group. Evidence of this is the absence of absorption peaks (corresponding to new end groups) in the infrared spectrum of the fluorocarbon polymer after treatment by this process that are distinguishable from peaks from $—CF_3$ groups.

The improvement in stability of the fluorocarbon polymer following treatment by this process is indicated by comparing the performance of treated and untreated polymer in appropriate service or laboratory tests (as will be discussed more fully hereinafter) and noting the improvement obtained for the treated polymer. This same improvement is observed for the polymers having molecular weights too high for the end group chemical changes to be seen by infrared analysis, but because the improvement is so obtained the chemical changes are believed to have occured.

The source of fluorine radicals may be any compound which generates these radicals under the conditions, mainly heating, employed. Such compounds are well-known in the art and by way of example include fluorine, CoF_3, AgF_2, UF_6, OF_2, N_2F_2, CF_3OF and the interhalogen fluorides, e.g., IF_5 and ClF_3.

The fluorocarbon polymers which are stabilised according to the present invention are the high molecular weight polymers which are normally solid and capable of being molded into articles, such as film, which are flexible and tough. Thus, the fluorocarbon polymers included herein are of a much higher molecular weight than the molecular weights of greases and/or waxes. The number average molecular weight of the fluorocarbon polymer is usually at least 10,000 and, generally, greater than 25,000. The fluorocarbon polymers also have a carbon atom in the main polymer chain beta to the unstable end group. In general, the main polymer chain, except for end groups, of these fluorocarbon polymers consists of carbon atoms. Any substituents on the main polymer chain, including side chains pendant therefrom, are such that they do not cause degradation of the polymer chain upon exposure to the fluorine radicals in the present invention. Preferably, these substituents are inert to fluorine radicals, so that the reaction with fluorine radicals is essentially limited to the end groups. To meet these criteria, the substituents will be such that the fluorocarbon polymer is either perfluorinated or highly fluorinated wherein the substituents other than fluorine, e.g., Cl and CF_3 are present at no greater frequency than every other carbon atom in the main polymer chain.

Representative fluorocarbon polymers stabilized in the present invention include the polymers derived from chlorotrifluoroethylene or tetrafluoroethylene and the copolymers of either of these monomers with one or more other copolymerizable monomers. Usually the principal monomer will be tetrafluoroethylene and the other copolymerizable monomer can include such monomers as the perfluorinated monomers such as hexafluoropropylene, disclosed in U.S. Patent No. 2,946,763 to Bro et al., the perfluoroalkenes containing from 4 to 10 carbon atoms, the perfluoro (alkyl vinyl ethers) such as perfluoro(propyl or ethyl vinyl ether) disclosed in U.S. Patent No. 3,132,123 to Harris et al. and perfluoro - (2 - methylene - 4 - methyl - 1,3 - dioxolane) disclosed in U.S. Patent No. 3,308,107 to Selman et al., and includes the highly fluorinated monomers, i.e., in which a single hydrogen substituent remains which does not change the fluorination character of the polymer, such as the 2-hydroperfluoroalkenes of 3 to 10 carbon atoms, e.g., 2-hydropentafluoropropene, the omega-hydroperfluoroalkenes of 3 to 10 carbon atoms, and the omega - hydroperfluoroalkyl perfluorovinyl ethers, the alkyl group having from 1 to 5 carbon atoms. Generally, sufficient of the comonomer is present to render the polytetrafluoroethylene melt fabricable; however, lesser or greater amounts but usually between 1 and 40 per cent by weight based on the weight of the copolymer can be present. In the case of the copolymer with hexafluoropropylene, from 5 to 35 per cent of units derived from this comonomer is preferred. For the remaining monomers, 1 to 20 per cent by weight is preferred.

Additional fluorocarbon polymers that can be stabilized according to the present invention are the fluorocarbon polymers which have groups pendant from the polymer chain. These pendant groups can be groups which are reactive or nonreactive toward fluorine radicals in the present process. In one embodiment of the present invention, the pendant groups are either ionic groups such as $—SO_3H$ or precursor groups convertible to $—SO_3H$. Such precursor groups are discussed below. It is preferred, though not essential, that the pendant precursor groups be nonreactive in the present process. The latter ionic groups preferably provide an ion exchange capacity of at least 0.3 milli-equivalents per gram of polymer. The preferred ionic group is $—SO_3H$. One class of such polymers with pendant precursor groups are the copolylmers of an ethylenically-unsaturated, sulfonyl fluoride-containing monomer and one or more of the

fluorocarbon polymer forming monomers hereinbefore described such as, for example, tetrafluoroethylene or chlortrifluoroethylene. Examples of these copolymers are those which are disclosed in U.S. Patent No. 3,041,317 to Gibbs et al. and U.S. Patent No. 2,282,875 to Connolly et al. and also U.S. Patent Application Serial No. 639,515, filed May 18, 1967 by Wolfe wherein the preparation and use of such polymers as ion exchange membranes in electrochemical cells, i.e., fuel cells and secondary electrochemical cells, is also disclosed. Examples of the monomer units in ion exchange membranes which are derived from the sulfonyl fluoride-containing monomer include

$$\begin{array}{l} \;\;| \\ CF_2 \\ \;\;| \\ FC{-}SO_3H \\ \;\;| \end{array}$$

and

$$\begin{array}{l} \;\;| \\ CF_2 \\ \;\;| \\ FC{-}(OCF_2CFY)_nOCF_2CR_fSO_3H \\ \;\;| \end{array}$$

wherein Y is F or CF_3, R_f is F or perfluoroalkyl having from 1 to 10 carbon atoms and n is an integer of 1 to 3 inclusive. Preferably the copolymer has from 0.5 to 50 mole per cent of the sulfonic acid containing units and an equivalent weight (weight of average repeat unit) of from 260 to 20,000, but more preferably from 800 to 2000. The preferred comonomer is tetrafluoroethylene. When the sulfonic acid is pendant directly from the main polymer chain, preferably a third monomer unit is present in the polymer, perfluoro(alkyl vinyl ether). It should be noted that copolymerization is not the only manner in which a polymer chain with pendant ionic groups or precursors thereto can be produced. Thus, such groups can be attached to an existing fluorocarbon polymer chain by grafting or chemical substitution.

While ion exchange membranes of this particular class of fluorocarbon polymer have high stability to temperatures up to about 250°C. and to acidic conditions at these temperatures, it has been found that after prolonged use in the hydrogen/oxygen fuel cell, HF appears in the water effluent from the fuel cell. The strongly reactive species, the hydroxyl radical, is believed to be present and degrade the membrane to give the HF. Treatment of this class of fluorocarbon polymers by the process of the invention improves the stability of the polymers and appears to solve this problem arising out of this utility.

Turning to a more detailed discussion of process conditions, the process of the present invention can be conducted by bringing the fluorine radical generating compound and the fluorocarbon polymer into intimate contact with one another at elevated temperature if such is required for generation of fluorine radicals by the compound. The temperature at which this process is conducted will therefore depend on the temperature at which this generation occurs for the particular fluorinating compound being used and on the reaction rate, short of degradation, desired. Generally, the temperature will be between 20° and 300°C.

The fluorocarbon polymers treated according to the present invention are in the solid state (not molten) during treatment. The solid state can be in the particulate or pre-molding form or in the molded form; the thicker the section, however, the longer is the treatment time required. Oxygen is excluded from the reaction system.

When the fluorine radical generating compound is gaseous, e.g., F_2 or UF_6, intimate contacting with the fluorocarbon polymer can be obtained by maintaining the polymer in an atmosphere of the fluorine radical generating compound for such time that the fluorine radicals permeate the solid polymer and give the end group conversion desired. An inert gas, e.g., N_2, can be present for dilution of the fluorine.

In the case of fluorine radical generating compounds which are solid at reaction conditions, e.g., CoF_3 and AgF_2, intimate contact with the fluorocarbon polymer may be obtained by dissolving or dispersing the fluorinating agent in an organic liquid which is inert to fluorine radicals and which wets the surface of the polymer and bringing this liquid into contact with the polymer. Some swelling of the polymer may occur, but the liquid should not be one which dissolves the fluorocarbon polymer. Generally, the liquid to be inert will be one of the well-known perfluorocarbon liquids, e.g., hexafluoropropylene epoxide derived oils, hexafluoropropylene cyclic dimer and perfluorinated kerosene; selection of liquid to be used will be dependent on the particular polymer to be treated.

The fluorination can be done batchwise or continuously. For example, the fluorocarbon polymer can be passed in one direction and the contacting fluorine radical generating compound flowed countercurrently.

In the case of the fluorocarbon polymers such as polytetrafluoroethylene and its copolymer with hexafluoropropylene, the color of the polymer treated by the present process is improved, i.e., whiter, over that of the untreated polymer.

In the case of the fluorocarbon polymers having pendant ionic groups, when these are derived by copolymerization, the pendant ionic group is usually in the form of a precursor group which is stable to the fluorination of the present invention. When the pendant ionic group is hydroxy acid, the precursor group will generally have the formula $-SO_2M$,

wherein M is F, amide, or groups of the formula —OMe, wherein Me is an alkali metal or quaternary ammonium. Where M is F or amide, the pendant group is converted to $—SO_3H$ by first reacting with a strong base such as sodium hydroxide to form the corresponding salt and then reacting this salt with a strong inorganic acid such as hydrochloric acid, which gives the hydroxy acid form ($—SO_3H$) desired for ion exchange polymer. When M is —OMe (defined above), the pendant group is converted to $—SO_3H$ by reaction with a strong inorganic acid. These conversion processes are described in greater detail in U.S. Patent No. 3,282,875 to Connolly et al. When the pendant acid groups are in the acid fluoride form ($—SO_2F$) the fluorocarbon polymer is readily melt fabricable; however, the hydroxy acid form is not as readily fabricable from a melt. For this reason, it is generally desirable to fluorinate (according to the present invention) fluorocarbon polymers wherein the pendant groups are acid fluoride ($—SO_2F$), then melt fabricate the resultant polymer with fluorinated end groups and pendant $—SO_2F$ into the shape desired, and finally convert the latter into the hydroxy acid form ($—SO_3H$).

The duration of the reaction will depend on such factors as the particular end groups being converted and their degree of conversion and on the particular reaction conditions and reaction system being employed. Preferably, the conversion is quantitative. However, applications arise where the degree of stabilization obtained by quantitative conversion is not necessary. Thus, the process can be conducted to a conversion of at least 40 per cent of the unstable end groups to stable end groups, but preferably to a conversion of at least 75 per cent. In the case wherein the molecular weight of the fluorocarbon polymer is such that the unstable end groups are reasonably visible in the infrared spectrum, the degree of conversion can be determined by end group count by standard infrared analysis techniques on samples (treated and untreated) of fluorocarbon polymer particles pressed into a film about 10 mil thick at a temperature of 350°C. for 5 minutes, except for the fluorocarbon polymers having pendant ionic groups on which a pressing temperature of 240°C. is used. In the case wherein the molecular weight of the fluorocarbon polymer is so high that infrared analysis is not applicable, the degree of conversion can be determined by comparing the amount of gas evolved from treated and untreated samples by subjecting the samples to an elevated temperature short of degration at which the gas evolution from the untreated sample appears greatest. An example of this gas evolution test is set forth in Example 30.

The PEROXIDE TEST referred to in the following examples is conducted as follows: a 0.5 to 1.5 g. sample of the fluorocarbon polymer being tested is dried in a vacuum oven at 100°C. for one hour, weighted and placed in a 25 mm. by 200 mm. test tube. To the test tube is then added 50 ml. of 30 per cent H_2O_2 containing 0.0025 g. of dissolved $FeSO_4 \cdot 7H_2O$. The test tube is heated up to 85°C. over a period of 1 hour and held at that temperature for 20 hours, followed by cooling to room temperature, decantation of the liquid contents of the test tube and rinsing of the interior of the test tube and polymer contents twice with 20 cc. charges of distilled water. The polymer is removed from the test tube, blotted dry and heat dried under the same conditions as the drying at the beginning of the test. The dried sample is then weighed, with the weight loss being a measure of end groups attacked by reaction of the polymer with the peroxide/ferrous ion solution. This procedure can be repeated and the average weight loss/cycle obtained.

The fluorocarbon polymers treated according to process of the present invention are useful in the same manner as the untreated polymers, except that where stability is a problem, use of the treated polymer is preferred.

The process of the present invention is illustrated by the following Examples in which parts and percents are by weight unless otherwise indicated.

EXAMPLES 1 to 11

In these Examples, the fluorocarbon polymer was the copolymer of tetrafluoroethylene with the monomer

$$FSO_2CF_2CF_2OCF(CF_3)CF_2OCF=CF_2$$

copolymerized essentially following the procedure of Example 8 of U.S. Pat. No. 3,282,875 to Connolly et al., except that the initiator was perfluoropropionyl peroxide, the polymerization temperature was 45°C., and the solvent was "Freon" 113. Three different molecular weights, as indicated by melt flow, of this copolymer were prepared. Polymer A had a melt flow of 342.5, Polymer B had a melt flow of 146.4, and Polymer C had a melt flow of 113.0. Melt flow was measured in grams of flow in 10 min. at 250°C. using a 5000 g. piston (.371 in. dia.) forcing the copolymer through an orifice of 0.0825 in. dia. by 0.315 inch long. This procedure of melt flow measurement is used in the remaining Examples herein, with some changes as indicated .

The fluorination procedure was as follows: samples of Polymers A, B and C were charged into nickel-lined shaker tubes (320 cc. capacity) which were then evacuated and purged with N_2 three times and evacuated a fourth time and pressured with 5 psig. of fluorine gas and heated under autogenous pressure for 2 hours. The tubes were then cooled to room temperature and the fluorine gas vented. Details of

these experiments and results are tabulated in Table I. For Examples 1—5 and 9—11, the polymer charged to the shaker tube was in the form of irregularly shaped granules measuring from about 1/64 to 1/4 inch diameter. The polymer charge for Examples 6—8 was in the form of film 5 mil thick.

The results of the fluorination treatment, is seen by comparing the end group count by infrared spectral analysis made on samples of the same polymers not fluorinated (Examples 1, 6 and 9) with the end group count on the fluorinated samples. In all cases, the number of unstable end groups is drastically reduced. The notation "N.D." in Table 1 means none detected. The limits of detection of the infrared equipment employed is believed to be as follows: (per 10^6 carbon atoms in the polymer) 5 end groups of carboxylate, monomer or dimer, and 10 vinyl end groups. The improvement in stability of the fluorinated polymers is seen by the large average reduction in weight loss per cycle of the PEROXIDE TEST as compared to the unfluorinated controls. The weight loss results are based upon from 3 to 6 cycles for each example.

TABLE I

Example	Polymer	Charge (g) to Shaker Tube	Equiv. Weight	Fluorination Conditions	End Groups/10^6 C Atoms			Peroxide Test
					Carboxylates Monomer	Dimer	$CF = CF_2$	Weight Loss (mgm)/Cycle
1	A	—	1210	None	625	565	255	17
2	A	50	1230	100°C.—2 Hr.	N.D.	N.D.	N.D.	2.0
3	A	50	1230	150°C.—2 Hr.	N.D.	N.D.	N.D.	1.3
4	A	50	1201	190°C.—2 Hr.	N.D.	N.D.	N.D.	2.5
5	A	25	1195	−50°C.—2 Hr. + 100°C.—2 Hr. + 150°C.—2 Hr.	N.D.	N.D.	N.D.	1.7
6	B	—	1335	None	662	520	109	16
7	B	50	1360	100°C.—2 Hr.	N.D.	N.D.	N.D.	3.3
8	B	29	1275	50°C.—2 Hr. + 100°C.—2 Hr. + 150°C.—2 Hr.	37	18	N.D.	6.0
9	C	—	1265	None	565	550	171	21
10	C	50	1300	190°C.—2 Hr.	N.D.	N.D.	N.D.	1.5
11	C	25	1225	190°C.—2 Hr.	23	6	N.D.	1.5

N.D. means none detected.

EXAMPLE 12

Into a 320 ml stainless steel shaker tube was charged 60 g. of Polymer A of Example 1, and 80 ml of FC-75 perfluorocarbon cyclic ether solvent containing 30 g. of CoF_3 dispersed therein. The contents were heated for 3 hours at 200°C. and the cobalt residue removed by washing with 10 per cent HCl in ethanol. The washed polymer had an equivalent weight of 1500. The end group count for the polymer prior to fluorination is given in Table I (Example 1). After fluorination by this example, no end groups could be detected in the infrared spectrum of the polymer.

A film of the fluorinated polymer was pressed and hydrolyzed to convert the pendant $-SO_2F$ groups to $-SO_3H$ groups. The hydrolysis procedure was to immerse the film for 24 hours in a 10 per cent NaOH solution at 80±10°C. The film was then water rinsed and soaked in three successive solutions of 10 per cent H_2SO_4 at room temperature (3 hrs. per soak). The film was then washed with distilled water until the pH of the wash water exceeded 4.5 after standing for one hour. The film was air dried and then subjected to the PEROXIDE TEST (7 cycles). The actual weight loss/cycle was 1 mgm. as compared to 17 mgm/cycle for the unfluorinated control.

EXAMPLES 13 to 18

Samples of tetrafluoroethylene/hexafluoropropylene (about 16 per cent hexafluoropropylene) in the form of a fine powder was charged into a series of shaker tubes, followed by alternately evacuating and purging with N_2 three times. The tubes were then evacuated once again and pressurized to 5 psig. with fluorine at room temperature, followed by placing the tubes in a shaker assembly, shaking and heating to the reaction temperature desired over a period of about 1 hour. Details of the polymer charge, temperature and time of fluorination and results are given in Table II.

The end group conversion results reported in Table II were determined by end group count using the infrared spectrum of each of the polymer samples. Volatiles index is a measure of the evolution of gas from the polymer at a given temperature, which reflects the stability of the polymer. From Table II it will be noted that the volatiles index is highest for Example 13 which was not fluorinated and decreases fairly progressively with increasing end group conversion. Improvement in color of the polymer follows the same trend, with the unfluorinated polymer being off-white and the 100 per cent end converted polymer being the whitest. Improvement in extrudability also follows the same trend, with the unfluorinated extruding as a foam (bubbles from unstable end groups) and with the amount of bubbles diminishing with increasing end group conversion.

TABLE II

Example	Polymer Charge gms	Temp. °C	F_2 Pressure Psig	Run Time Hrs.	End Group Conv. %	Melt Viscosity × 10^{-4} Poises at 360°C. 5 min.	15 min.	30 min.	Volatiles Index
13			none			4.7	5.5	5.6	95—100
14	100	150	15	2	30	7.3	8.5	9.0	68
15	100	200	20	3	75	7.5	7.8	7.8	53
16	100	250	20	2	100	5.1	5.2	5.0	28
17	150	225	20	2	75	6.9	7.5	7.2	34
18	150	225	20	2	100	9.3	9.4	7.2	—

EXAMPLE 19

Example 16 is repeated sufficiently to accumulate about 600 g. of fluorinated polymer which was extruded through a 1 inch extruder, cut into molding cubes which were then divided into three samples. The melt viscosity stability of the extruded cubes was unchanged from the initial determination immediately after extrusion, after 8 days, and after 17 days. This uniformity in melt viscosity over a period of time shows the storage stability of the polymer obtained by the fluorination treatment.

EXAMPLES 20 to 26

In these experiments a series of fixed beds of 20 g. each of the copolymer powder of Examples 12—18 were established, each being heated up to the temperature desired by flowing N_2 through the bed, followed by flowing mixtures of F_2 and N_2 through the bed. Each bed was also heated by a heating jacket at 240 to 250°C. Temperatures of the F_2—N_2 gas mixture, duration of the run and results of these experiments are given in Table III. The per cent conversion of end groups was 100 per cent for each of these runs.

TABLE III

Example	Temp. °C.	Mole % F_2 in N_2	Time Min.	Melt Viscosity $\times 10^{-4}$ Poises at 360°C. 5 min.	10 min.	15 min.	Volatiles Index
20	200—250	20	16	3.2	3.7	3.6	40
21	195—210	20	5	3.6	3.6	3.5	45
22	183	4	37	5.6	6.0	6.2	37
23	192—197	4	15	6.9	6.5	6.4	48
24	204—213	4	5	5.6	5.9	5.6	50
25	212—215	4	18	6.9	7.1	6.9	39
26	200—205	8	20	7.6	7.6	7.6	39

EXAMPLE 27

A copolymer of tetrafluoroethylene/perfluoro-(propyl vinyl ether)/trifluorovinylsulfonyl fluoride was prepared as follows: to a 250 ml. flask containing about 20 g. of MgO was charged 163 g. of trifluorovinylsulfonyl fluoride and 24 g. of perfluoro (propyl vinyl ether). The resultant mixture was distilled under vacuum into a 300 cc. heavy wall polymerization bottle to which was added 1 cc. of perfluoropropionyl peroxide in "Freon" 113 (3×10^{-3} molar) (Freon is a trade mark). Air was removed by cooling the contents and evacuating the bottle, followed by warming the evacuated bottle to room temperature and then introducing small amounts of tetrafluoroethylene while increasing the temperature of the bottle to 45°C. The tetrafluoroethylene pressure was increased to 40 psig. and held at this pressure for 5 hrs. The pressure was then allowed to decrease to 27 psig., followed by cooling the bottle to −78°C. and pumping off unreacted tetrafluoroethylene. The bottle was warmed to room temperature and the volatile contents were distilled off yielding 179 g. of residue which was washed with about 200 ml. of "Freon" 113 filtered and dried for 2 hrs. at 150°C. under vacuum to yield 15.0 g. of copolymer containing units of each of the monomers present, as seen in the infrared spectrum of the copolymer. The copolymer had 6.2 per cent trifluorovinylsulfonyl fluoride, an equivalent weight of about 1700 and 153 end groups of carboxylate dimer and 475 vinyl end groups per 10^6 C atoms.

The copolymer was fluorinated following the

procedure of Example 3, except that the polymer charge was 7.7 g. instead of 50 g. After fluorination, the equivalent weight appeared unchanged and no end groups were detected in the infrared spectrum of the copolymer.

EXAMPLE 28

The copolymer of Example 9 was converted to the sodium carboxylate sulfonyl fluoride form by heating 50 g. of it together with 15 g. of $NaOAc.H_2O$ and 200 ml of glacial acetic acid to reflux in a flask overnight, with stirring. The resultant copolymer was filtered, washed with about 500 ml. of distilled water, dried overnight and then at 125°C. in a vacuum oven. The copolymer had an equivalent weight of 1265 and 182 and 131 carboxylate end groups, monomer and dimer respectively, and 99 vinyl end groups, all per 10^6 C atoms.

The copolymer was then fluorinated following the procedure of Example 3, except that the polymer charge was 25 g. After fluorination, no end groups were detected in the infrared spectrum of the copolymer.

EXAMPLE 29

A copolymer of tetrafluoroethylene/perfluoro(propyl vinyl ether) was prepared by charging to a polymerization vessel 75 g. of perfluoro(propyl vinyql ether) 4200 ml H_2O, 6 g. ammonium persulfate, 15 g. ammonium carbonate, 220 g. paraffin and 10 g. of ammonium perfluorooctanate. The vessel was then pressurized with methane to 25 psig., followed by pressurizing with tetrafluoroethylene up to 275 psig. at 70°C. for 92 minutes accompanied by agitation at 125 rpm. For each 250 g. of tetrafluoroethylene added during the polymerisation run, 5 ml. of the vinyl ether and 7 psig. of methane were also added. The washed copolymer recovered from the polymerization vessel contained 1.7 per cent of polymerised perfluoro(propyl vinyl ether) and had a melt viscosity of 33.5 × 10^4 poises at 380°C. In the infrared spectrum of the copolymer amide end groups were the only end groups detectible and it was estimated that there were about 140 of these per 10^6 C atoms.

Following the fluorination procedure of Example 3, except using a 100 g. charge, a temperature of 250°C. and a F_2 pressure of 36 psig., only 21 end groups are detected by infrared analysis.

EXAMPLE 30

Commercially available polytetrafluoroethylene granular polymer (average particle size 20 microns) was fluorinated in a shaker tube at 250°C. for 1/2 hour, using a mixture of 8 mol per cent F_2 in N_2. The fluorinated polymer was molded into a chip at 3000 psi. molding pressure, sintered at 420°C. for 2 hours and cooled to 270°C. at the rate of 1.07°C/min. The inherent specific gravity as measured by infrared analysis of the polymer in the chip was 2.2258 g/cc. The inherent specific gravity of the polymer (control) after identical treatment except no fluorination, was 2.2333. The lower specific gravity of the fluorinated polymer, indicating higher molecular weight, indicates the improved stability thereof over the control polymer.

1.46 g. of the fluorinated tetrafluoroethylene granular polymer and the same amount of the same polymer (control) but not fluorinated were each heated at 410°C. for 1/2 hour under a vacuum of 10^{-3} mm. Hg to determine how much gas was evolved, which was indicated by an increase in the pressure of the systems. The control polymer gave off about 2-1/2 times the amount of gas evolved from the fluorinated polymer, indicating the greater stability of the fluorinated polymer and a conversion of about 60 per cent of the unstable groups.

EXAMPLE 31

Following the procedure of Example 29, except that no ammonium buffer was used, gave a copolymer of tetrafluoroethylene/perfluoro(propyl vinyl ether) having a melt viscosity of 122 × 10^4 poises at 360°C., 2.2 per cent vinyl monomer derived units, and 117 carboxylate end groups per 10^6 C atoms.

The copolymer was fluorinated according to the procedure of Example 3, except that the polymer charge was 25 g. The resultant copolymer has 13 carboxylic end groups.

WHAT WE CLAIM IS:—

1. A process for chemically stabilising a solid high molecular weight fluorocarbon polymer (as herein defined) which contains chemically unstable end groups which comprises contacting the solid polymer in the absence of oxygen, with a source of fluorine radicals under conditions at which said source generates fluorine radicals, whereby at least 40% of the chemically unstable end groups are converted to chemically stable end groups.

2. A process according to claim 1 wherein the fluorocarbon polymer is polytetrafluoroethylene, tetrafluoroethylene/hexafluoropropylene copolymer or a tetrafluoroethylene/perfluoro (alkyl vinyl ether) copolymer.

3. A process according to claim 1 wherein the fluorocarbon polymer contains one or more groups, pendant from the main polymer chain, of the formula $—SO_2M$ wherein M is F, amide or OMe where Me is an alkali metal or quaternary ammonium group.

4. A process according to claim 1 wherein the fluorocarbon polymer is in the form of an ion exchange resin, said polymer having pendant from the main polymer chain $—SO_2F$ groups, wherein the polymer is first treated with said source of fluoride radicals under conditions at which said source generates fluorine radicals, and then said $—SO_2F$ groups are converted into $—SO_3H$ groups.

5. A process according to claim 4 wherein the resin is in the form of a membrane.

6. A process according to claim 4 or 5 wherein the fluorocarbon polymer is a copolymer of tetrafluoroethylene or chlorotrifluoroethylene and an ethylenically unsaturated sulfonyl fluoride-containing monomer.

7. A process according to any preceding claim wherein the fluorinated polymer has a number average molecular weight of at least 10,000.

8. A process according to claim 7 wherein the fluorinated polymer has a number average molecular weight of greater than 25000.

9. A process according to claim 1 or 2 substantially as herein described in any of the Examples.

10. Fluorocarbon polymers stabilised by the process of any of claims 1 to 9.

11. Ion exchange membranes stabilised according to the process of claim 5.

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